

## PATENT ABSTRACTS OF JAPAN

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(54) ENGINE VALVE MADE OF TI ALLOY OF INTERNAL COMBUSTION ENGINE HAVING WEAR RESISTING FLAME SPRAYED LAYER OF EXCELLENT THERMAL SHOCK RESISTANCE

(57)Abstract:

PURPOSE: To restrain generation of crazing and cracking and ensure wear resistance for a long term by providing a wear resisting flame sprayed layer of specific average thickness out of the surface coating Ti powder of construction in which an Al coating layer is formed on the surface of Ti powder through a Ni coating layer, on the slide face of and the contact face with the valve guide and the valve seat of the valve main body of an engine valve made of Ti alloy.

CONSTITUTION: A valve main body is constituted out of a precision casting of composition of Ti 60% AlV wt.%, and for example the size is set so as to be 22.5mm in the diameter of valve head, 4.5mm in the stem diameter, and 92mm in the length. Fixed depth of cut in the range 150-500 $\mu$ m is formed by cutting on the extreme end face of the valve head part contacting with a valve seat and the outer circumferential face of the center stem part slidingly contacting with a valve guide. For flame spray material, for example, powder in which WC powder of average particle size 37 $\mu$ m is mixed with Cr<sub>3</sub>C<sub>2</sub> powder of 40 $\mu$ m size, Ti powder of 44 $\mu$ m size, Al powder of 40 $\mu$ m size in weight ratio 63:37, is used. Next, flame spraying is executed to the depth of cut face by plasma gas, so as to form a wear resisting layer of average thickness. Hereby, thermal shock resistance and close fitness to the valve main body can be also improved.

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TITLE: Titanium@ alloy engine valve for internal combustion for wear resistant layer - comprises valve guide, sliding surface and mating surface of body coated with hot sprayed titanium@ powder and aluminium@ and nickel@ layers

PATENT-ASSIGNEE: MITSUBISHI MATERIALS CORP[MITV]

PRIORITY-DATA: 1995JP-0106866 (April 6, 1995)

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ABSTRACTED-PUB-NO: JP 08284621A

BASIC-ABSTRACT:

The valve guide, sliding surface, and mating surface of engine valve body are coated by wear resistant layer having average thickness of 0.15-0.5 mm, formed by hot spraying of Ti powder coated by Al layer by Ni layer.

ADVANTAGE - The Ti alloy engine valve for internal combustion engine having high wear resistant hot sprayed layer.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: TITANIUM@ ALLOY ENGINE VALVE INTERNAL COMBUST WEAR RESISTANCE

LAYER COMPRISE VALVE GUIDE SLIDE SURFACE MATE SURFACE BODY COATING

HOT SPRAY TITANIUM@ POWDER ALUMINIUM@ NICKEL@ LAYER

DERWENT-CLASS: M13 Q51

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**CLAIMS**

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[Claim(s)]

[Claim 1] The engine valve made from Ti alloy of the internal combustion engine which has the thermal shock resistance excellent in the wear-resistant-spraying layer characterized by preparing the wear-resistant-spraying layer formed in a sliding surface and a contact side with a valve guide and a valve seat at least, using the surface coating Ti powder which has the structure of the engine valve body made from Ti alloy which formed aluminum enveloping layer through nickel enveloping layer on the front face of Ti powder as thermal-spraying material by 150-500-micrometer average thickness.

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[Translation done.]

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

**[Industrial Application]** This invention relates to the engine valve made from Ti alloy of the internal combustion engine excellent also in abrasion resistance and adhesion while having the thermal shock resistance excellent in the wear-resistant-spraying layer.

**[0002]**

**[Description of the Prior Art]** As an internal combustion engine's bulb made from Ti alloy so that it may be indicated by the former, for example, JP,1-197067,A, and JP,4-21756,A by for example, weight % The engine valve made from Ti alloy which has the typical presentation of Ti-6%aluminum-4%V at least to a sliding surface and a contact side with a valve guide and a valve seat WC powder and Cr<sub>3</sub> C<sub>2</sub> The thing which comes to prepare powder and the wear-resistant-spraying layer formed further, using the mixed powder of Ti powder and aluminum powder as thermal-spraying material by 100-500-micrometer average thickness is known.

**[0003]**

**[Problem(s) to be Solved by the Invention]** On the other hand, in the above-mentioned engine valve made from a conventional Ti alloy, although the service condition of the engine valve which be the structural member of this tend to increase cruelty much more with the high increase in power of an internal combustion engine in recent years, and high performance-izing, since especially a wear resistant spraying layer be a thing possessing sufficient thermal shock resistance, when the severe thermal shock by the heat cycle of heating and cooling at the time of engine operation be receive, it be easy to generate a crack and a crack in this, and there be a problem in respect of dependability.

**[0004]**

**[Means for Solving the Problem]** As a result of inquiring from the above viewpoints paying attention to the wear-resistant-spraying layer in an internal combustion engine's engine valve made from Ti alloy in order to aim at this improvement in thermal shock resistance, this invention person etc. then, as thermal-spraying material On the front face of Ti powder and Ti powder which has the mean particle diameter of 40-70 micrometers desirably First all by the mechanical plaiting method etc. nickel enveloping layer If it forms by 5-10-micrometer average thickness desirably and a wear-resistant-spraying layer is further formed using the surface coating Ti powder which comes to form aluminum enveloping layer by 5-10-micrometer average thickness desirably on this As for the wear-resistant-spraying layer of this result, a Ti-nickel intermetallic-compound layer exists between Ti core part and nickel interlayer. It has the structure to which the nickel-aluminum intermetallic-compound layer existed between said nickel interlayer and aluminum periphery layer. And since it consisted of a mutual welding object of the multiplex layer structure particle which carried out flattening at the time of a thermal-spraying side collision, the research result of coming to provide the adhesion which was excellent with aluminum of a periphery layer, the thermal shock resistance which was excellent with multiplex layer structure, and the abrasion resistance which was excellent with the intermetallic-compound layer was obtained.

**[0005]** This invention is made based on the above-mentioned research result. The engine valve body

made from Ti alloy at least to a sliding surface and a contact side with a valve guide and a valve seat. The wear-resistant-spraying layer formed using the surface coating Ti powder which has the structure which formed aluminum enveloping layer in the front face of Ti powder through nickel enveloping layer as thermal-spraying material. It has the description in the engine valve made from Ti alloy of the internal combustion engine which has the thermal shock resistance excellent in the wear-resistant-spraying layer which it comes to prepare by 150-500-micrometer average thickness, and was excellent also in abrasion resistance and adhesion.

[0006] In addition, in the engine valve of this invention, when that average thickness cannot continue the abrasion resistance of a request in less than 150 micrometers at a long period of time, and it cannot secure but that average thickness exceeds 500 micrometers on the other hand, it is from the reason especially for becoming easy to generate exfoliation under severe conditions to have determined the average thickness of a wear-resistant-spraying layer as 150-500 micrometers, and its 150-300-micrometer average thickness is desirably good. Moreover, the mean particle diameter of Ti powder which constitutes this about thermal-spraying material is desirable to be referred to as 40-70 micrometers as above-mentioned. This is the case where Ti core part in the multiplex layer structure particle to which the mean particle diameter constitutes a wear-resistant-spraying layer from less than 40 micrometers disappears arises, and the fall of the thermal shock resistance by the fall of a multiplex number of layers is not avoided but the mean particle diameter exceeds 70 micrometers on the other hand. It is what is depended on the reason the rate of Ti core part occupied in a wear-resistant-spraying layer increases too much, and abrasion resistance comes to fall. Further the average thickness of nickel enveloping layer. Although it is desirable to be referred to as 5-10 micrometers as above-mentioned, this becomes insufficient [less than 5 micrometers] forming [of the Ti-nickel intermetallic-compound layer formed at the time of thermal spraying] the average thickness. Desired abrasion resistance is not only securable, but thermal shock resistance comes to fall with reduction of the multiplex number of layers by nickel interlayer's disappearance. It is from the reason the rate of on the other hand occupying in nickel interlayer's wear-resistant-spraying layer if the average thickness exceeds 10 micrometers increases too much, and abrasion resistance comes to fall. Having set same desirable average thickness of aluminum enveloping layer to 5-10 micrometers as above-mentioned. Formation of a nickel-aluminum intermetallic-compound layer is inadequate like [the average thickness / in less than 5 micrometers] the case of nickel enveloping layer. The fall of the thermal shock resistance by disappearance of aluminum periphery layer and the fall of the adhesion to an engine valve body are not avoided except that desired abrasion resistance is not obtained. On the other hand, when the average thickness exceeds 10 micrometers, it is based on the reason the rate of aluminum periphery layer occupied in a wear-resistant-spraying layer increases too much, and abrasion resistance comes to fall.

[0007]

[Example] Below, an example explains the engine valve of this invention concretely. First, it consists of a precision casting casting which had the presentation of Ti-6%aluminum-4%V by weight % as an engine valve body. diameter of umbrella part: -- 22.5mmx shaft diameter: -- 4.5mmx die-length: -- with the umbrella part apical surface which has the dimension of 92mm and contacts a valve seat. The engine valve body made from Ti alloy which comes to form the infed of the predetermined depth within the limits of 150-500 micrometers by cutting was prepared for the valve guide and the shank central outside peripheral surface which slides. Moreover, the surface coating Ti powder prepared by forming nickel enveloping layer of the average thickness shown in Table 1 using nickel powder of a mean diameter similarly shown in Table 1 by each with usual mechanical plating equipment in the front face of Ti powder which has a mean diameter as shown in Table 1 as thermal-spraying material, and forming aluminum enveloping layer as shown in Table 1 still the more nearly same on this was prepared. moreover, the comparative purpose -- as thermal-spraying material -- mean-particle-diameter:37micrometer WC powder -- said -- 40-micrometer Cr<sub>3</sub> C<sub>2</sub> powder and mean-particle-diameter:44micrometer Ti powder -- said -- the mixed powder which 63:37 comes out comparatively and comes to mix 40-micrometer aluminum powder by the weight ratio was prepared.

[0008] In subsequently, the condition of having masked except said thermal-spraying side on the

thickness:0.2mm Teflon tape, to the thermal-spraying side (infeed side) of the above-mentioned engine valve body 4 kgG/cm<sup>2</sup> Blasting processing is performed with a discharge pressure using an alumina shot. The field granularity is set to Ra 5-20. To this Plasma current:400A, Plasma electrical potential difference : 70V, amount of plasma gas:50 l/min, and thermal-spraying travel-speed:30 m/min, Thermal-spraying material speed of supply: 25g / min By forming the wear-resistant-spraying layer of average thickness which performs thermal spraying on conditions and is shown in Table 1, the engine valve made from this invention Ti alloy (It is hereafter called this invention bulb) The engine valves 1-3 made from Ti alloy (conventionally henceforth a bulb) were manufactured 1-5, and conventionally, respectively.

[0009] Next, the valve guide made the various bulbs obtained as a result the product made from steel casting, operation of 100 hours was performed on the conditions to which the valve seat made the nest and the engine speed 4000r.p.m. which is severe conditions at 2500 cc gasoline engine of 6-cylinder made from Cu alloy, and the maximum wear depth in the wear-resistant-spraying layer of a valve-guide sliding surface and a valve-seat contact side, and a crack and the number of crack initiation were measured. These measurement results were shown in Table 1.

[0010]

[Table 1]

種 別		溶 射 材					耐 摩 耗 溶 射 層				
		Ti粉末の 平均粒径 ( $\mu$ m)	Ni被覆層		Al被覆層		平均層厚 ( $\mu$ m)	バルブガイド滑動面		バルブシート当接面	
			使用Ni粉末 の平均粒径 ( $\mu$ m)	平均層厚 ( $\mu$ m)	使用Al粉末 の平均粒径 ( $\mu$ m)	平均層厚 ( $\mu$ m)		最大摩耗 深さ ( $\mu$ m)	割れ・亀裂 発生数 (本)	最大摩耗 深さ ( $\mu$ m)	割れ・亀裂 発生数 (本)
本 発 明 バ ル ブ	1	44	3.1	5.4	2.6	5.1	150	17	0	18	0
	2	44	3.1	7.9	2.6	7.3	200	15	0	16	0
	3	44	3.1	9.6	2.6	9.5	300	13	0	15	0
	4	67	3.1	5.3	2.6	5.6	400	16	0	18	0
	5	67	3.1	9.2	2.6	9.6	500	18	0	19	0
従 来 バ ル ブ	1	WC粉末					250	82	7	43	8
	2	Cr <sub>1</sub> C <sub>2</sub> 粉末					250	69	7	37	6
	3	Ti粉末とAl粉末の混合粉末					250	58	9	62	10

[0011]

[Effect of the Invention] There is neither a crack from which this invention bulbs 1-5 all show [ result / which is shown in Table 1 ] bulbs 1-3, an EQC, or the outstanding abrasion resistance beyond this conventionally, and generating is not conventionally avoided by bulbs 1-3 in spite of operation under severe conditions, nor crack initiation, and it is clear to have the outstanding thermal shock resistance. As mentioned above, since the engine valve made from Ti alloy of this invention has the thermal shock resistance excellent in the wear-resistant-spraying layer which constitutes this and is excellent also in abrasion resistance and the adhesion to an engine valve body, even if operation of an internal combustion engine is performed under severe conditions, neither a crack nor crack initiation is in this, and it demonstrates the abrasion resistance which continued and was excellent in the long period of time.

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(54) 【発明の名称】 耐摩耗溶射層がすぐれた耐熱衝撃性を有する内燃機関のTi合金製エンジンバルブ

## (57) 【要約】

【目的】 耐摩耗溶射層がすぐれた耐熱衝撃性を有する内燃機関のTi合金製エンジンバルブを提供する。

【構成】 内燃機関のTi合金製エンジンバルブが、Ti合金製エンジンバルブ本体の少なくともバルブガイドおよびバルブシートとの摺動面および当接面に、Ti粉末の表面にNi被覆層を介してAl被覆層を形成した構造の表面被覆Ti粉末を溶射材として用いて形成した耐摩耗溶射層を、150～500μmの平均層厚で設ける。

## 【特許請求の範囲】

【請求項1】 Ti合金製エンジンバルブ本体の少なくともバルブガイドおよびバルブシートとの摺動面および当接面に、Ti粉末の表面にNi被覆層を介してAl被覆層を形成した構造を有する表面被覆Ti粉末を溶射材として用いて形成した耐摩耗溶射層を、150～500μmの平均層厚で設けたことを特徴とする耐摩耗溶射層がすぐれた耐熱衝撃性を有する内燃機関のTi合金製エンジンバルブ。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】この発明は、耐摩耗溶射層がすぐれた耐熱衝撃性を有すると共に、耐摩耗性および密着性にもすぐれた内燃機関のTi合金製エンジンバルブに関するものである。

## 【0002】

【従来の技術】従来、例えば特開平1-197067号公報および特開平4-21756号公報に記載されるように、内燃機関のTi合金製バルブとして、例えば重量%で、Ti-6%Al-4%Vの代表的組成を有するTi合金製エンジンバルブの少なくともバルブガイドおよびバルブシートとの摺動面および当接面に、WC粉末やCr<sub>3</sub>C<sub>2</sub>粉末、さらにTi粉末とAl粉末の混合粉末を溶射材として用いて形成した耐摩耗溶射層を、100～500μmの平均層厚で設けてなるものなどが知られている。

## 【0003】

【発明が解決しようとする課題】一方、近年の内燃機関の高出力化および高性能化に伴ない、これの構造部材であるエンジンバルブの使用条件は一段と苛酷さを増す傾向にあるが、上記の従来Ti合金製エンジンバルブにおいては、特に耐摩耗溶射層が十分な耐熱衝撃性を具備するものでないため、エンジン移動時の加熱・冷却の熱サイクルによるきびしい熱衝撃を受けると、これに割れや亀裂が発生し易く、信頼性の点で問題がある。

## 【0004】

【課題を解決するための手段】そこで、本発明者等は、上述のような観点から、内燃機関のTi合金製エンジンバルブにおける耐摩耗溶射層に着目し、これの耐熱衝撃性向上をはかるべく研究を行なった結果、溶射材として、Ti粉末、望ましくは40～70μmの平均粒径を有するTi粉末の表面に、いずれもメカニカルプレーティング法などにて、まずNi被覆層を、望ましくは5～10μmの平均層厚で形成し、さらにこの上にAl被覆層を、望ましくは5～10μmの平均層厚で形成してなる表面被覆Ti粉末を用いて、耐摩耗溶射層を形成すると、この結果の耐摩耗溶射層は、Ti芯部とNi中間層の間にTi-Ni金属間化合物層が存在し、前記Ni中間層とAl外周層の間にNi-Al金属間化合物層が存在した構造をもち、かつ溶射面衝突時に偏平化した多重

層構造粒子の相互融着体からなることから、外周層のAlによってすぐれた密着性、多重層構造によってすぐれた耐熱衝撃性、および金属間化合物層によってすぐれた耐摩耗性を具備するようになるという研究結果を得たのである。

【0005】この発明は、上記の研究結果にもとづいてなされたものであって、Ti合金製エンジンバルブ本体の少なくともバルブガイドおよびバルブシートとの摺動面および当接面に、Ti粉末の表面にNi被覆層を介してAl被覆層を形成した構造を有する表面被覆Ti粉末を溶射材として用いて形成した耐摩耗溶射層を、150～500μmの平均層厚で設けてなる、耐摩耗溶射層がすぐれた耐熱衝撃性を有し、かつ耐摩耗性および密着性にもすぐれた内燃機関のTi合金製エンジンバルブに特徴を有するものである。

【0006】なお、この発明のエンジンバルブにおいて、耐摩耗溶射層の平均層厚を150～500μmと定めたのは、その平均層厚が150μm未満では所望の耐摩耗性を長期に亘って確保することができず、一方その平均層厚が500μmを越えると、特に苛酷な条件下では剥離が発生し易くなるという理由からであり、望ましくは150～300μmの平均層厚がよい。また、溶射材に関して、これを構成するTi粉末の平均粒径は、上記の通り40～70μmとするのが望ましく、これは、その平均粒径が40μm未満では耐摩耗溶射層を構成する多重層構造粒子におけるTi芯部が消失する場合が生じ、多重層数の低下による耐熱衝撃性の低下が避けられず、一方その平均粒径が70μmを越えると、耐摩耗溶射層に占めるTi芯部の割合が多くなりすぎて耐摩耗性が低下するようになるという理由によるものであり、さらにNi被覆層の平均層厚は、上記の通り5～10μmとするのが望ましいが、これは、その平均層厚が5μm未満では、溶射時に形成されるTi-Ni金属間化合物層の形成が不十分となり、所望の耐摩耗性を確保することができないばかりでなく、Ni中間層の消失による多重層数の減少に伴なって耐熱衝撃性が低下するようになり、一方その平均層厚が10μmを越えるとNi中間層の耐摩耗溶射層に占める割合が多くなりすぎて耐摩耗性が低下するようになるという理由からであり、同じくAl被覆層の望ましい平均層厚を、上記の通り5～10μmとしたのは、その平均層厚が5μm未満では、Ni被覆層の場合と同様にNi-Al金属間化合物層の形成が不十分で、所望の耐摩耗性が得られないほか、Al外周層の消失による耐熱衝撃性の低下およびエンジンバルブ本体への密着性の低下が避けられず、一方その平均層厚が10μmを越えると耐摩耗溶射層に占めるAl外周層の割合が多くなりすぎて耐摩耗性が低下するようになるという理由にもとづくものである。

## 【0007】

【実施例】つぎに、この発明のエンジンバルブを実施例

により具体的に説明する。まず、エンジンバルブ本体として、重量％でTi-6%Al-4%Vの組成をもった精密鑄造鋳物からなり、傘部径：22.5mm×軸径：4.5mm×長さ：92mmの寸法を有し、かつバルブシートと当接する傘部先端面と、バルブガイドと摺動する軸部中央部外周面に、150～500μmの範囲内の所定の深さの切込みを切削加工により形成してなるTi合金製エンジンバルブ本体を用意した。また、溶射材として、表1に示される通りの平均粒径を有するTi粉末の表面に、いずれも通常のメカニカルプレーティング装置にて、同じく表1に示される平均粒径のNi粉末を用いて表1に示される平均層厚のNi被覆層を形成し、さらにこの上に同じく表1に示される通りのAl被覆層を形成することにより調製した表面被覆Ti粉末を用意した。また、比較の目的で、溶射材として、平均粒径：37μmのWC粉末、同40μmのCr<sub>3</sub>C<sub>2</sub>粉末、および平均粒径：44μmのTi粉末と同40μmのAl粉末を重量比で63：37の割合で混合してなる混合粉末を用意した。

【0008】ついで、上記エンジンバルブ本体の溶射面（切込み面）に、前記溶射面以外を厚さ：0.2mmのテ\*

\*フロンテープでマスキングした状態で、4kgf/cm<sup>2</sup>の吐出圧でアルミナショットを使用してブラスト処理を施して、その面粗さをRa5～20とし、これに、プラズマ電流：400A、プラズマ電圧：70V、プラズマガス量：50l/min、溶射走行速度：30m/min、溶射材供給速度：25g/minの条件で溶射を行って表1に示される平均層厚の耐摩耗溶射層を形成することにより本発明Ti合金製エンジンバルブ（以下、本発明バルブという）1～5および従来Ti合金製エンジンバルブ（以下、従来バルブという）1～3をそれぞれ製造した。

【0009】つぎに、この結果得られた各種バルブを、バルブガイドが鋳鋼製にして、バルブシートがCu合金製の6気筒2500ccガソリンエンジンに組込み、エンジン回転数を苛酷な条件である4000r.p.m.とした条件で100時間の運転を行ない、バルブガイド摺動面およびバルブシート当接面の耐摩耗溶射層における最大摩耗深さと、割れ・亀裂の発生数を測定した。これらの測定結果を表1に示した。

【0010】

【表1】

種 別		溶 射 材					耐 摩 耗 溶 射 層				
		Ti粉末の 平均粒径 ( $\mu\text{m}$ )	Ni被覆層		Al被覆層		平均層厚 ( $\mu\text{m}$ )	バルブガイド滑動面		バルブシート当接面	
			使用Ni粉末 の平均粒径 ( $\mu\text{m}$ )	平均層厚 ( $\mu\text{m}$ )	使用Al粉末 の平均粒径 ( $\mu\text{m}$ )	平均層厚 ( $\mu\text{m}$ )		最大摩耗 深 さ ( $\mu\text{m}$ )	割れ・亀裂 発 生 数 (本)	最大摩耗 深 さ ( $\mu\text{m}$ )	割れ・亀裂 発 生 数 (本)
本 発 明 バ ル ブ	1	44	3.1	5.4	2.6	5.1	150	17	0	18	0
	2	44	3.1	7.9	2.6	7.3	200	15	0	16	0
	3	44	3.1	9.6	2.6	9.5	300	13	0	15	0
	4	67	3.1	5.3	2.6	5.6	400	15	0	18	0
	5	67	3.1	9.2	2.6	9.6	500	18	0	19	0
従 来 バ ル ブ	1	WC粉末					250	82	7	43	8
	2	Cr <sub>3</sub> C <sub>2</sub> 粉末					250	69	7	37	6
	3	Ti粉末とAl粉末の混合粉末					250	58	9	62	10

【0011】

【発明の効果】表1に示される結果から、本発明バルブ1～5は、いずれも従来バルブ1～3と同等、あるいはこれ以上のすぐれた耐摩耗性を示し、かつ苛酷な条件下での運転にもかかわらず、従来バルブ1～3では発生が避けられない割れや亀裂の発生なく、すぐれた耐熱衝撃性を有することが明らかである。上述のように、この発明

※明のTi合金製エンジンバルブは、これを構成する耐摩耗溶射層がすぐれた耐熱衝撃性を有し、かつ耐摩耗性およびエンジンバルブ本体への密着性にもすぐれているので、内燃機関の運転が苛酷な条件下で行なわれても、これに割れや亀裂の発生なく、長期に亘ってすぐれた耐摩耗性を発揮するのである。